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CONTENTS

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Sludge deposition and caustic embrittlement in the pre-mature failure of a waste heat boiler steel plate

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A failure investigation of a welded waste heat boiler steel shell that developed transverse cracks was carried out in 1996 to determine the cause of failure as well as propose measures to be adopted to prevent similar failures occurring in the future. The boiler had been in service for several years before two cracks across two traversing circumferential welds were discovered on the underside during routine inspection. Chemical and metallographic analyses indicated that the boiler plate was made from a conventional C-Mn steel and that it was certainly suitable for the purpose. The boiler interior showed massive deposition of a calcareous sludge on the walls and tube bundles. This was attributed to an excessive use of sodium orthophosphate to reduce the hardness of the boiler feed water. The high levels of Na^+ and PO_4^{3-} ions found in both the sludge and boiler feed water analyses were taken as confirmatory evidence. Feed water quality monitored data for the period January 1994 to October 1995 showed pH values that were in excess of 12.4, a figure much higher than the recommended pH range of 8 to 11. The high pH is thought to have been responsible for the occurrence of cracking as a result of caustic embrittlement. This point of view is supported by the observation of intergranular separation in the microstructures adjacent to the crack paths.

Keywords: *sludge deposition, pH control, waste heat boiler, intergranular, crack path.*

Introduction

The design of boilers and related steam-power plant equipment is inherently conservative to the extent that in some cases fabrication defects that may be present do not cause failure to occur until after a considerable period of operation. As with other steam-power plant equipment, boilers are subject to a variety of failures involving one or more of several mechanisms. Most prominent among these are corrosion, mechanical-environment processes, fatigue related fractures and distortion arising mainly from thermal-expansion or creep effects. When corrosion is the major cause of failure, the active corrosion agent is not always obvious. In this regard, the collection and preservation of corrosion products, particularly loose, flaky or powdery deposits is important. Subsequent chemical analysis of such

corrosion products often becomes the key factor in the elucidation of the cause of failure (Nancollas, 1983; Hartt *et al.*, 1984; French, 1986; Syrett, 1987; Kunjapur *et al.*, 1987; Lin and Dexter, 1988; Luo *et al.*, 1991; Mantel, *et al.*, 1992).

As with most investigations, the general aim in analysis of failure in boilers is to understand the root cause of the failure in terms of both material and boiler operational conditions (Hartt *et al.*, 1984; Tapping *et al.*, 1991; Puckorius and Brooke, 1991). This article discusses the failure analysis of a waste heat boiler shell that had been in service for five years before transverse cracks were observed to have developed across two circumferential welds. In the analysis, emphasis is placed on the distinctive features that characterise the mode of failure, hence a determination of the cause. On the basis of this information suggestions for corrective measures are proposed.

Materials and Methods

A welded steel plate containing the cracks was cut from the underside position of a waste heat boiler steel shell that developed transverse cracks across circumferential welds. A schematic representation of the positions of cracks with respect to the circumferential welds is shown in Figure 1a. A section containing the 46 mm long crack was cut into six segments and these were further subdivided into two along the weld (Figure 1b). The chemical composition of steel plate used to fabricate the boiler shell was determined quantitatively by spectrographic technique using a specimen labelled segment 1' (Figure 1b) in which the weldment and base metal were both present. The analysis obtained is given in Table 1.

Table 1: Chemical analysis of base steel plate and weldment

	C	Si	Mn	P	S
Weldment	0.090	0.046	0.830	0.006	0.016
Plate	0.200	0.340	0.830	0.003	0.008

Visual inspection of boiler interior

An inspection of the boiler interior showed massive deposition of a calcareous sludge of varying thickness (1 to 3.5mm) on heat exchange tubes as well as on the inside walls of the boiler underside. Where the sludge had been dislodged/removed on account of mechanical damage, the steel plate surface was found to be covered by a thin adherent magnetite layer. Cracking of steel plate was also observed.

Chemical analysis of sludge deposit and boiler water

The composition of the sludge as well as that of the boiler feed water supplied was determined by wet chemical method and the results are shown Table 2.

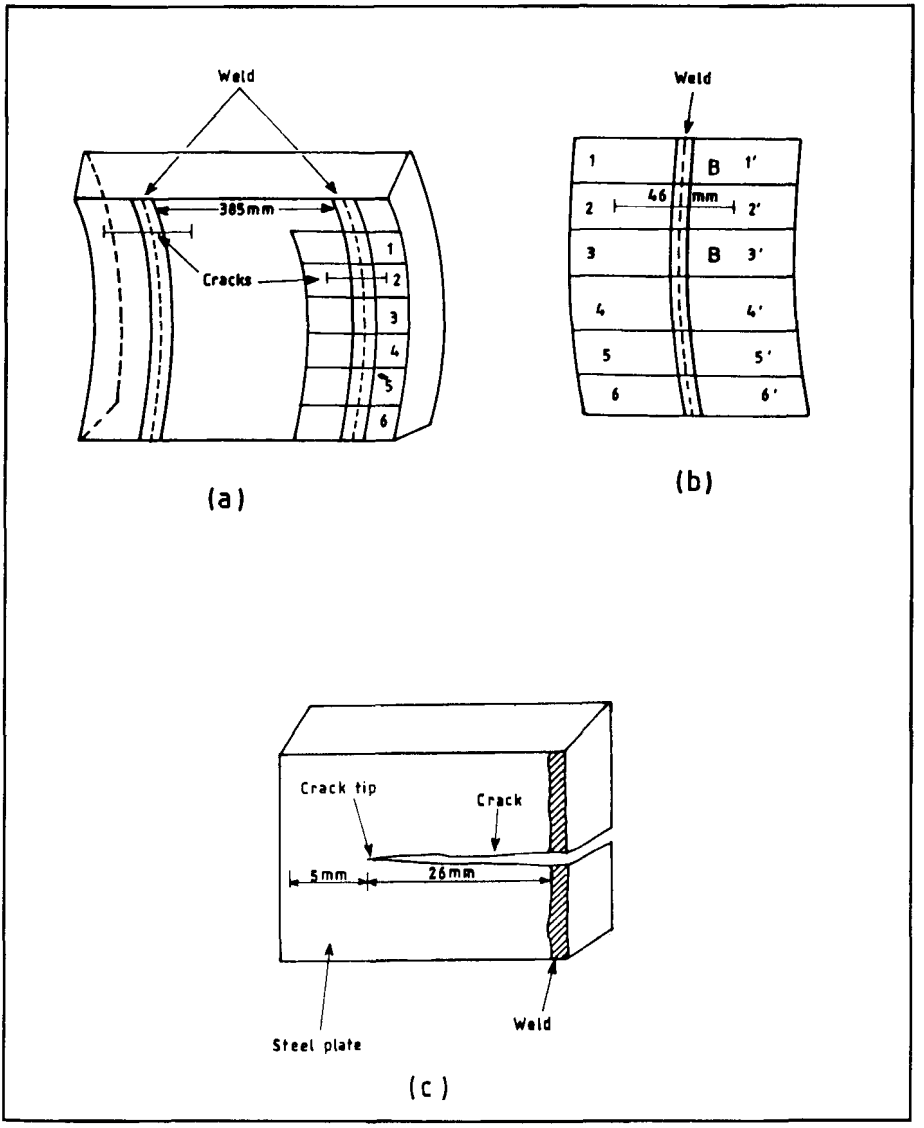

Figure 1: Schematic representation of the boiler steel plate showing:

(a) dimensions and position of two transverse cracks relative to the two circumferential welds.

(b) section with the shorter of the two cracks sub-divided into six segments.

(c) segment used in microhardness profile determination (see Figure 5).

Macro- and microscopic examination
A low magnification examination of the fracture surface of the mating halves after cutting segment 2' at B-B' (Figure 1b) was carried out using a STEMI SV optical microscope. Specimen samples for microstructural analysis included sections of the weldment and the area adjacent to the cracks and crack tips (see segment 2 in Figure 1b). The samples, after polishing were etched in 2 percent nital. The Zeiss IM35 microscope fitted with a 35 mm camera was used to examine and document the microstructural features observed on the polished specimens in their unetched and etched conditions.

Microhardness measurements
The Vicker's (mini-load) micro-hardness tester using a load of 4.90N was used to determine the hardness profile along the main crack edge and crack tip (see Figure 1c).

Plant monitored data
Plant monitored data with respect to the variation of pH, caustic alkalinity, chlorides, phosphates, conductivity and total dissolved solids taken over a period of five years (February 1991 to February 1996) prior to the discovery of cracking of the boiler shell steel plate was also be used to further discuss the feed water quality control problems leading to the premature failure.

Results

Macroscopic observations
A close examination of the surface after removing the magnetite did not reveal features characteristic of general corrosion. The two cracks previously observed on the outside were also identified on the water-side after removing the calcareous sludge and magnetite scale/film. This provided clear evidence that through cracking of the steel plate across both welds had occurred.

A low magnification examination of the fracture surface of the mating halves after cutting open segment 2' at B-B' (Figure 1b) showed a fracture surface that appeared brittle and was characterised by shinny facets arising possibly from some form of intergranular separation. This observation and the absence of any visible signs to suggest 'plastic deformation' is indicative of brittle fracture as being operative in the cracking process.

Chemical analysis of weldment and steel plate
The chemical analysis of the weldment and base metal (Table 1) show a manganese content of about 0.83 weight percent. With such a manganese level, a slight dilution of the pearlite is expected so that the eutectic point would be slightly low compared with 0.8 percent in the Fe-C alloy. The sulphur and phosphorous analyses were found to be well below the maximum permissible levels for weldable steels. The steel used to fabricate the boiler shell is a conventional C-Mn steel and is certainly

suitable for the purpose. Its intrinsic hardness was found to be 220 HV, a value that would imply good ductility, toughness and adequate strength for the purpose.

Microstructure and microhardness analyses

Examination of the weld/base metal interface, that is, the weld fusion zone in the unetched condition (see segments 1', 3' to 16' in Figure 1b) did not reveal the presence of such defects as slag inclusions or pores indicating that good welding practice had been followed. After etching the specimens in 2 percent nital solution, two different microstructures were , however, observed. These comprised 'white' or 'light' and 'dark' zones (Plate 1). When both zones were viewed at high magnifications, the 'white' zone was found to consist of columnar and equiaxed grains labelled A and B, respectively. The dark zone marked C in Plate 1 shows the microstructure to be martensite. In constrast, the base metal away from the weld fusion zone had a pearlite-ferrite microstructure with some of the pearlite appearing in clusters (Plate 2). It is most probable that in the dark zone of the weld/base metal interface, the pearlite was transformed into martensite/bainite, which is inherently brittle unless tempered. Microhardness measurements taken of these structures showed the following trends: 'white' zone, 213 to 219 HV and 'dark' zone, 234 to 253 HV. Plates 3 and 4 show the section of the crack previously indentified as segment 2' (Figure1b) viewed from the water-side in the unetched and etched conditions, respectively. Several cracks branching from the main crack can be seen (Plate 3). Blunting of the main crack tip is also evident. The mode of cracking appears to predominantly intergranular (Plate 4). The observation of intergranular separation in the microstructure reported suggests the possible involvement of caustic embrittlement in the cracking process, a point that will be discussed later in the light of the chemistry of the sludge and boiler feed water.

Microhardness measurements taken on the segment identified as 2 in Figure 1b show the hardness values adjacent the main crack path ranging between 254 and 363 HV. A plot of the Vickers hardness, HV, versus distance from the weld to a point ahead of the crack tip is shown in Figure 2. The higher peaks in the curve were found to correspond to areas where there was a relatively high density of pearlite structures in the area in or adjacent to the crack path. Ahead of the crack tip, the hardness was found to drop rather rapidly down to a value of approximately 225 HV as the distance from the crack tip was increased. This value is in agreement with the general hardness of 220 HV for this material as reported earlier.

Analysis of plant monitored data

Graphical analyses of plant monitored boiler feed water quality control data with respect to the variation of pH, caustic alkalinity, chlorides, phosphates, conductivity and total dissolved solids taken over a period of five years (February 1991 to February 1996) are shown in Figures 3 to 8. The points displayed in each graph indicate the maxima, minima and mean values attained. It would, however, appear from the graphs that data point separation (time period between plotted points)

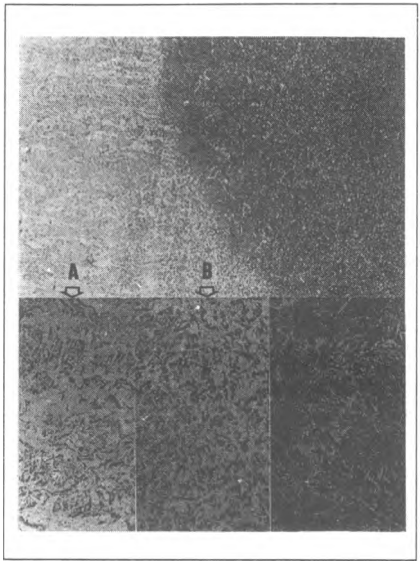

Plate 1: Microstructure of the weld/base metal interface. x100
(i) White zone: A — columnar and B — equiaxed grains. x200
(ii) Dark zone: C— martensite. x200

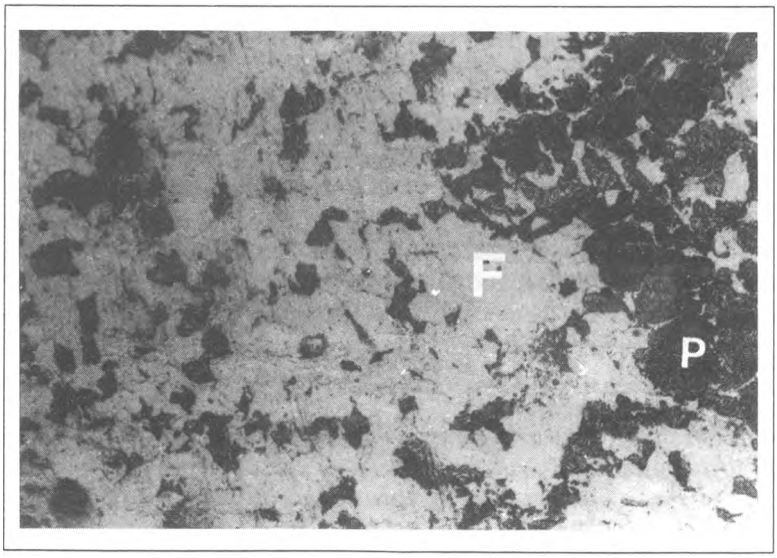

Plate 2: Microstructure of the base steel plate away from the weld. x100

Plate 3: A section of the segment designated 2' in Figure 3b viewed from the waterside in the unetched condition showing: M-main crack; B and C-branching cracks; blunt crack tip. x100

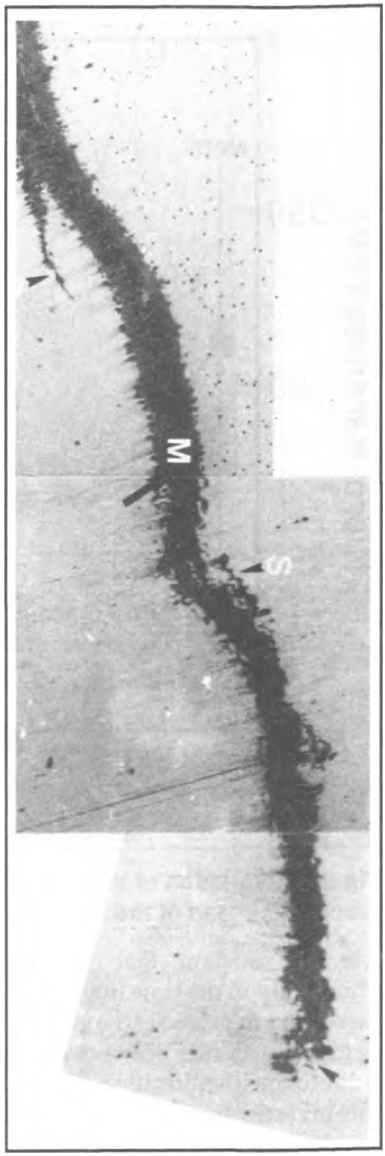

Plate 4: Microstructure of the main branching crack described in Figure 6 showing intergranular separation, S. x200

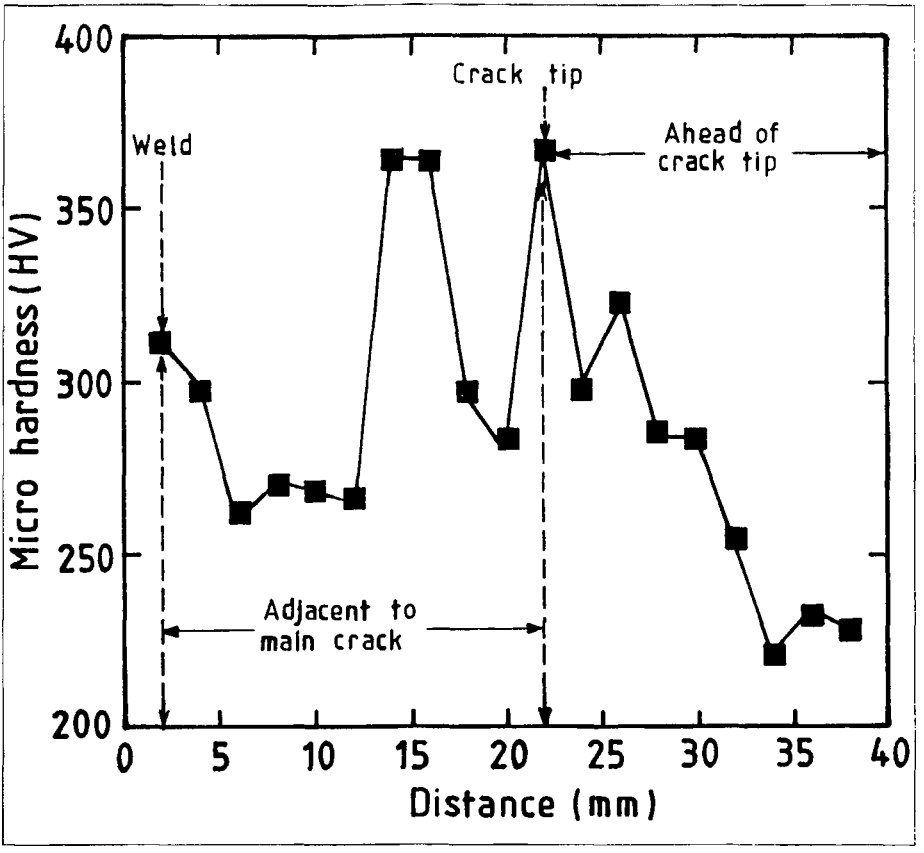

Figure 2: Variation of Vickers microhardness with distance adjacent the main crack and ahead of the crack tip.

was not constant, that is, it varied from three to seven months. The lack of uniformity in the time intervals between plotted readings makes it difficult to use these data to properly monitor boiler feed water quality. This obviously affects the degree of accuracy of any corrective measures likely to have been taken. The period prior to the identification of the cracking problem which seems most significant in this investigation lies between June 1994 and February 1996. An analysis of the pH graph during this period, for example, shows that the latter was generally maintained on the high side with maximum values of around 12.4 being reported(Figure 3). A pH range of 8 to 11 is suggested in the literature [Brown, 1971]. The optimum pH level for a system which is established by experience for each installation is the level that keeps amounts of corrosion products of iron in the boiler at a minimum. However, with inadequate water treatment practice or laxed pH control, there is potential for excessive water-side corrosion, in particular on boiler tube surfaces.

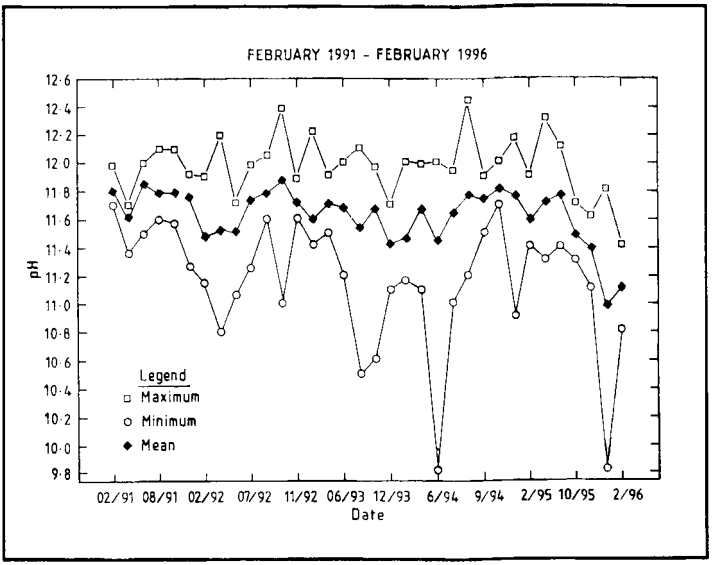

Figure 3: Variation of boiler feed water pH during the period February 1991 to February 1996.

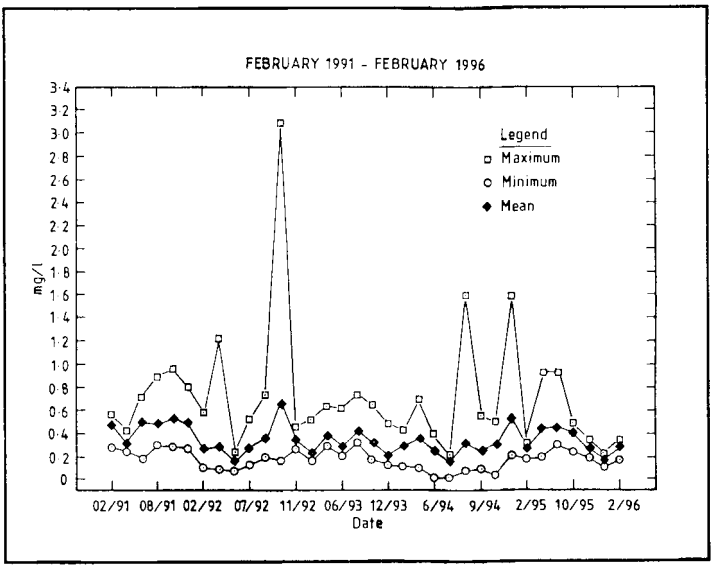

Figure 4: Variation of boiler feed water caustic alkalinity during the period February 1991 to February 1996.

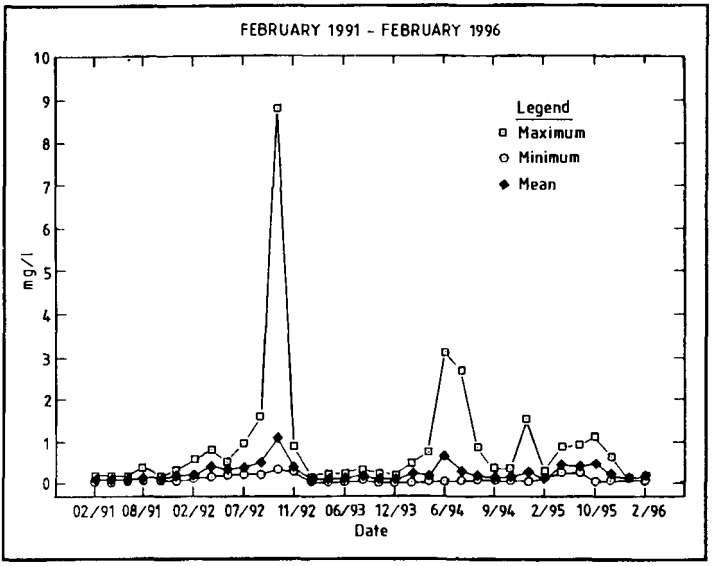

Figure 5: Variation of boiler feed water chloride content during the period February 1991 to February 1996.

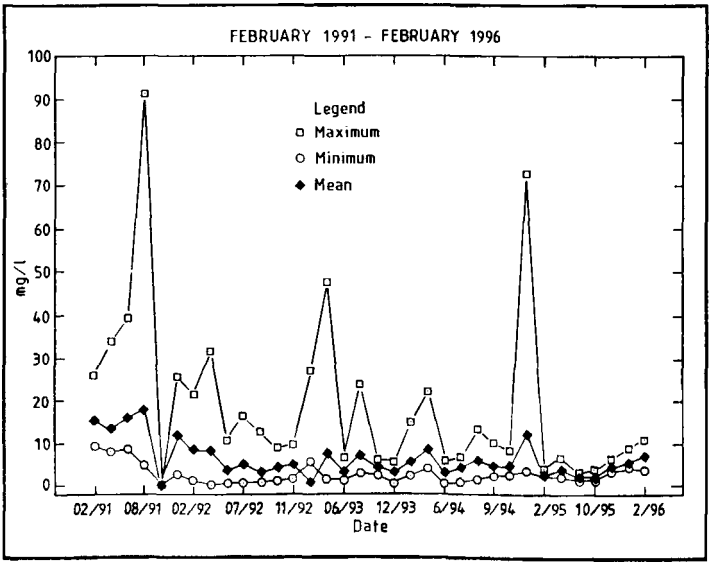

Figure 6: Variation of boiler feed water phosphate content during the period February 1991 to February 1996.

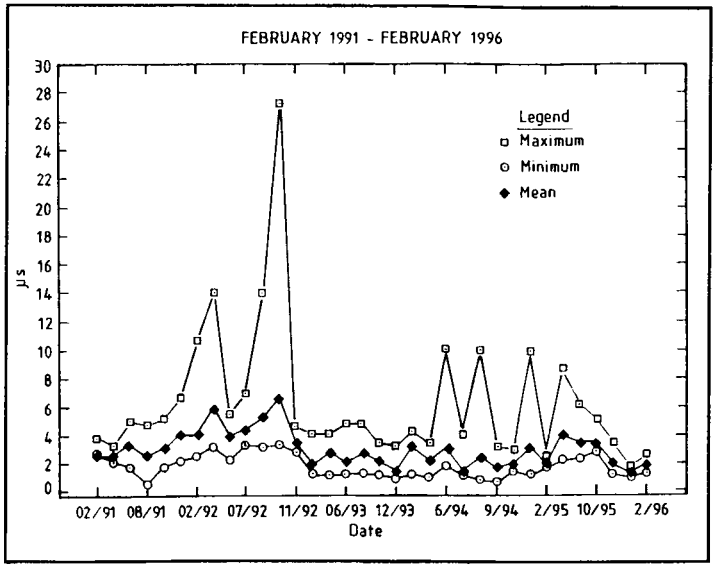

Figure 7: Variation of boilder feed water conductivity during the period February 1991 to February 1996.

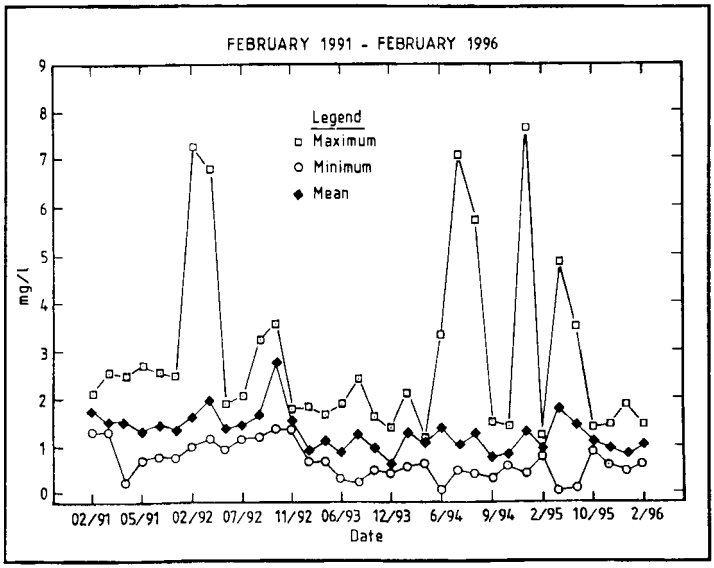

Figure 8: Variation of boiler feed water total dissolved solids during the period February 1991 to February 1996.

The corresponding alkalinity, chloride and phosphate values (Figures 4 to 6) for the period under consideration were within acceptable ranges. Conductivity and total dissolved solids on the other hand were generally on the high side (Figures 7 and 8).

Analysis of sludge and boiler feed water

Table 2: Chemical analysis of sludge and boiler feed water

	Sludge deposit	boiler feed water
pH	10.18	9.07
Cl^-	51 ppm	177 ppm
$CaCO_3$	9.1 % (as CO_3^{2-})	0.88 ppm
PO_4^{3-}	14.28 %	49.11 ppm
SO_4^{2-}	10.8 %	5.49 %
Fe^{3+}	1.47 %	0.10 %
Fe^{2+}	1.09 %	0.06 %
Ca^{2+}	11.0 %	2.1 ppm
Mg^{2+}	5.95 %	0.6 ppm
K^+	0.31 %	30 ppm
Na^+	47.9 %	77 ppm

The Mg^{2+}, Ca^{2+}, Na^+, PO_4^{3-}, SO_4^{2-} and $CaCO_3$ constituents in the sludge were found to be in fairly large proportions compared to Fe^{3+}, Fe^{2+} and K^+ (see Table 2 above). The low levels of Fe^{3+}/Fe^{2+} would seem to suggest that these originated from the protective magnetite layer that normally forms on steels on the water-side in the presence of residual oxygen and are therefore not a consequence of active corrosion. With the exception of SO_4^{2-}, Fe^{3+} and Fe^{2+} most of the constituents analysed for in boiler feed water were in ppm. Compounds containing Fe, Ca^{2+}, Mg^{2+} and Na^+ cations and the anions HCO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^- are normally present in most raw water. The compounds of Ca^{2+} and Mg^{2+} which are the known causes of water hardness become less soluble in water as the temperature is increased and at temperatures common in boilers they will usually precipitate as tube-wall deposits or hardness scale. The presence of high levels of Ca^{2+}, Mg^{2+} and PO_4^{3-} in the sludge is indicative of the occurrence of such a phenomenon particularly during the period June 1994 and October 1995 and may explain the high maxima in total dissolved solids reported in the boiler feed water analyses (Figure 8). This also explains the presence of a calcareous scale on the boiler wall and tube bundle surfaces previously described.

Discussion

The deposition of corrosion scale products or sludge to form scales on boiler wall surfaces and tube bundles results in poor heat transfer and this often leads to

overheating failures. In practice, the major source of water-side scale in boilers is not the deposition of corrosion products but that of dissolved solids in the feed water [Puckorius and Brooke, 1991; Trethewey and Chamberlain, 1995]. The observation of a high level of sludge formation points to a couple of issues: poor boiler feed water treatment; excessive use of sodium orthophosphate to treat hard waters without the accompanying 'blowing down' practice to remove the sludge that precipitates.

Control of pH which is achieved by adding either sodium hydroxide in conjunction with sodium hexametaphosphate or sodium orthophosphate to boiler feed water. This, perhaps explains the high levels of Na^+ and PO_4^{3-} reported (Table 2). In waters containing high levels of Ca^{2+} and Mg^{2+}, that is, hard waters (Lin and Dexter, 1988), the orthophosphate precipitates as sludge and this necessitates periodic 'blowing down' of the boiler to remove the residue. If left undisturbed, the sludge may deposit as a hardness scale onto boiler walls and tube bundles. Depending on the nature of the deposit, localised concentration corrosion cells are likely to set up under the deposit (Mantel *et al.*, 1992). The sodium levels can also be augmented by the use of sodium sulphite which oxidizes to sulphate when used to scavenge dissolved oxygen chemically. This view point is supported by the high SO_4^{2-} levels which were found in the sediment (Table 2).

Sometimes, the hardness scale formed by the deposition of sludge is somewhat porous (Tapping *et al.*, 1991). In this case, dissolved solids in the boiler water as well as alkalis introduced to treat the feed water can become concentrated in these pores. This often leads to severe pitting corrosion of the steel in areas immediately beneath the hardness scale. Pitting corrosion is initiated by the absorption of activating anions (particularly chloride ions) on defective sites in the normally protective magnetite layer. Figure 5 shows a slight increase in maximum chloride content of the feed water during the period January 1994 to October 1995. Subsequent analysis of the sludge showed a chloride content of about 51 ppm, a figure three times less than that reported for the feed water (Table 2). The conditions within the pit can be very different from those existing in the bulk solution. Pit chemistry studies have reported values of pH as low as 1.7 (Brown, 1971). Depending on pit density and the stress state of the steel, some pits can become initiation sites for stress corrosion cracks by acting as stress raisers. Very low concentrations of the chloride ions are required for pit initiation. Assuming hydrogen is liberated under the highly acidic conditions existing at the tip of the pit (crack), brittle fracture resulting from hydrogen embrittlement (also referred to as hydrogen induced cracking) can be a possible mechanism of failure.

Alternatively, the steel may fail on account of caustic embrittlement, another form of stress corrosion cracking which can occur in stressed low carbon steels in strong alkaline solutions such as those encountered in this work. It develops from the deposition of feed water products in which NaOH can concentrate to high pH levels where the protective Fe_3O_4 layer becomes soluble and rapid corrosion occurs. The caustic levels can concentrate from less than 100 ppm NaOH in the bulk

to over 200 000 ppm in the pores of the deposit adjacent to the boiler wall surface. In caustic embrittlement, crack propagation is generally intergranular. In the present investigation, high pH and caustic alkalinity reported in the period prior to the discovery of the two transverse cracks point strongly to the involvement of caustic embrittlement in the cracking process. The observation of intergranular separation in the microstructures adjacent to the crack paths provides further confirmation of the suggested failure mechanism.

Conclusion

An inspection of the interior of the boiler showed massive sludge deposition on boiler wall and heat exchange bundle tube surfaces. This was associated with excessive use of sodium orthophosphate in the treatment of feed water to reduce its hardness. The failure of the boiler steel plate by cracking is attributed to caustic embrittlement resulting from the high alkaline conditions that prevailed at the time. Caustic embrittlement can be prevented by one of several methods: anodic protection which forms a continuous stable oxide film or by cathodic protection which completely reduces the oxide film; adding strong oxidizing agents to passivate the steel surface; use of inhibitors such as nitrates, sulphates and phosphates. However, the adjustment of boiler water composition and the addition of inhibitors should be done only when the chemical behaviour of the material involved is fully understood and only after suitable laboratory testing because adjustment of boiler water composition can destroy effectiveness of inhibitors. Common practice for most steam boilers is to control pH. The corrosion resistance of plain carbon steels used in the manufacture of boilers depends on keeping the protective Fe_3O_4 layer in place by controlling the pH and amounts of deposit forming contaminants in the feed water supply magnetite is unstable and soluble at pH values below 5 and above 12.

Cracking which occurred on the underside was probably initiated by a simple combination of existing residual stresses and normal operational conditions from underneath a porous calcareous sludge deposit. Stress relieving after welding is advisable in order to avoid excessive residual stresses around the weld.

That caustic embrittlement appears most plausible as the cause of failure is supported by observation of intergranular features in the microstructures. Furthermore, the C-Mn steel which was used to fabricate the boiler shell is known to be susceptible to caustic cracking, particularly at elevated temperatures such as those encountered in waste heat boilers.

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